

PATENT SPECIFICATION

(11) 1212805

1212805

NO DRAWINGS

- (21) Application No. 10423/69 (22) Filed 26 Feb. 1969
 (31) Convention Application No. 12112
 (32) Filed 26 Feb. 1968 in
 (33) Japan (JA)
 (45) Complete Specification published 18 Nov. 1970
 (51) International Classification A 61 k 7/00
 (52) Index at acceptance

A5B 771

C5D 6B11A 6B11B 6B12A 6B12C 6B12L 6B12N1



(54) TRANSPARENT LIQUID COSMETIC COMPOSITION

(71) We, SANKYO COMPANY LIMITED, A Japanese Body Corporate of, 1-6 3-Chome, Nihonbashi-Hon-Cho, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a transparent, flowable cosmetic containing squalene, squalane and/or pristane.

In the cosmetic industry, a number of cosmetics of transparent solution type, such as nourishing facial lotion, cleansing facial lotion, hair shampoo, liquid hair dressing etc. have been widely manufactured and sold.

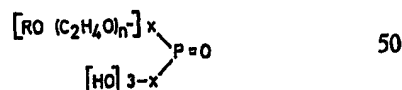
It has previously been attempted to incorporate the squalene compound into creams or milk lotions. Attempts have also been made to solubilize the squalene compound for a liquid cosmetic, for example, by ozonising said squalene compound to its water-soluble derivative. It has not so far been possible to obtain a transparent liquid having the squalene compound incorporated therein.

In view of the above, we have studied solubilizing agents which may solubilize the squalene compound so as to make it compatible with a transparent, liquid cosmetic. Some surface active agents can be used to solubilize the squalene compound in water, but generally the quantities required are so large as to be commercially impractical.

We have now found that when a surface active agent of the phosphoric acid ester type or of the higher fatty alcohol-polyoxyethylene ether type is added in small amount to a transparent aqueous cosmetic solution, the squalene compound can be solubilized easily in said solution. The resulting transparent solution can be added to any of those additives commonly employed in the art without losing its transparency.

The present invention therefore comprises a flowable cosmetic composition which comprises (a) at least one of squalene, squalane

and pristane, (b) at least one phosphoric acid ester-type surface active agent of the general formula



or a salt thereof, or a higher fatty alcohol-polyoxyethylene ether type surface active agent of the general formula:



wherein each R and R' represents a saturated or unsaturated aliphatic hydrocarbon radical of 10 to 18 carbon atoms, n is an integer from 3 to 10, x is an integer from 1 to 3, and y is an integer from 8 to 40, and (c) a liquid diluent.

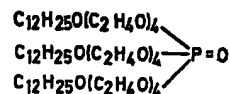
Squalene which is used in this invention is an unsaturated hydrocarbon of the empirical formula $\text{C}_{30}\text{H}_{50}$, which is found in large amount in the livers of shark, crocodile, etc., but also constitutes several per cent of human skin. This compound also plays an important role in metabolism as a precursor of cholesterol.

Squalane is the hydrogenation product of squalene. This compound is less oily than mineral hydrocarbons, has good penetration and lubrication for human skin and is readily emulsifiable.

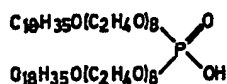
Pristane is aliphatic hydrocarbon of the empirical formula $\text{C}_{19}\text{H}_{40}$, which exists in the livers of fish, particularly shark, and has the same properties as those of squalane.

Typical surface active agents useful in this invention are illustrated below.

Phosphoric acid ester type 80

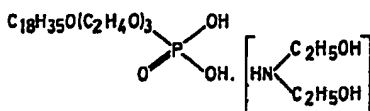


(Hostaphat KL 340, Registered Trade Mark, of Hoechst A.G., Germany)

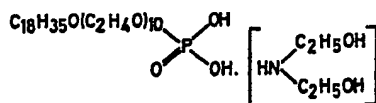


(Hostaphat KO 280),

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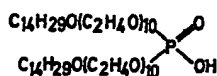


(Crodafos N3N, Registered Trade Mark, of Nippon Croda Co., Ltd., Japan)



(Crodafos N₁₀N)

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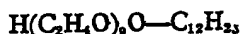
(Nikkol DLP 10, tradename of Nikko Chemicals Co., Ltd., Japan)

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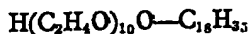
The salts of these phosphoric acid ester type surface active agents, for example, di-lower alkanolamine salts (e.g. diethanol amine salts) or alkali metal salts (e.g. sodium salts), also may be used.

Higher fatty alcohol-polyoxyethylene ether type

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(Nikkol BL-9, from Nikko Chemicals Co., Ltd., Japan)



25 (Brij 96, Registered Trade Mark of Kao-Atlas Co. Ltd., Japan or Volpo 10, Registered Trade Mark, of Nippon Croda Co., Ltd., Japan)



(Brij 98, from Kao-Atlas Co., Ltd., Japan)

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(Nikkol BL-15, from Nikko Chemicals Co., Ltd., Japan)



(Nikkol BL-25, tradename, of Nikko Chemicals Co., Ltd., Japan)

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Mixture of higher fatty alcohol-polyoxyethylene glycol ethers

(Eumulgin M8, Registered Trade Mark of Henkel International G.M.B.H., Germany)

Polyoxyethylene lanoline alcohol ethers

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(Solulan 16, tradename, of American Cholesterol Product Incorporation, U.S.A.)

The amount of the surface active agent to be used as a solubilizing agent for the squalene compound may vary depending on the type of said surface active agent but it usually is a small amount falling within the range of 1/2 to 6 parts per part by weight of the squalene compound. If the surface active agent is used in too large an excess, the resulting cosmetic will be a jelly, with poor fluidability, which has no commercial value. By the addition of said surface active agent, it is possible to obtain a transparent, liquid cosmetic containing 0.1—10% w/v of the squalene compound.

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It is very surprising that a transparent, flowable cosmetic having as high concentration of the squalene compound as about 10% w/v can be obtained using a small amount of the solubilizing agent. The resulting transparent, liquid cosmetic is a commercially valuable transparent cosmetic solution which is excellent in emulsifiability, penetration, hydrophilization, extendability, etc., whilst retaining the special effect of the squalene compound.

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The following examples illustrate the invention:

EXAMPLE 1

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| | |
|------------------|----------|
| Squalene | 1% w/v |
| Hostaphat KL 340 | 2 " |
| Glycerine | 5 " |
| Citric acid | 0.2 " |
| Sodium citrate | 0.2 " |
| Ethanol | 5 " |
| Perfume | Optional |

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The mixture of the squalene, the Hostaphat and perfume is warmed to about 70°—80°C. and a solution of the glycerine and the citric acid in water (at about 70°—80°C.) is gradually added thereto with stirring.

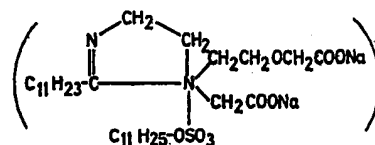
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To the resulting mixture is added the ethanol. Then, water is added in sufficient amount to make up total 100% w/v. A transparent nourishing facial lotion is obtained.

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EXAMPLE 5

| | | |
|------------------------|--------|----|
| Pristane | 3% w/v | 60 |
| Eumulgin M8 | 4 | " |
| Miranol 2 MCA modified | 30 | " |



| | | |
|-----------------|--------|----|
| Hexylene glycol | 2% w/v | |
| Amisol LDE | 1 " | 65 |

(Lauryl monoethanolamide, of Nikko
Chemicals Co., Ltd., Japan)

The mixture of the squalane, the pristane, the Crodafos and the Volpo is warmed to about 80°—90°C. To the warmed mixture is added about one-tenth volume of water (at about 80°—90°C.), based upon the total volume of the finished lotion, with stirring. After cooling, the resulting mixture is dissolved in the remaining portion of the water and to the solution is added a solution of the methylparaben and the propylparaben in the ethanol. Then, the allantoin, the propylene glycol and the Solulan are successively added to the mixture, which is then acidified to pH 5.0 by gradual addition of the lactic acid. Finally, water is added to make up total 100% w/v. A transparent nourishing facial lotion is obtained.

The mixture of the pristane, the Eumulgin, the Mironal and the Amisol is warmed to about 60°—70°C. To the warmed mixture is added an aqueous solution of the hexylene glycol (at about 60°—70°C.) After cooling, water is added to make up total 100% w/v. A transparent shampoo is obtained.

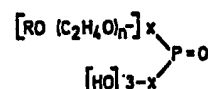
WHAT WE CLAIM IS:—

1. A flowable cosmetic composition which comprises (a) at least one of squalane, squalene and pristane, (b) at least one phosphoric acid ester-type surface active agent of the general formula

EXAMPLE 3

| | | |
|----|----------------|----------|
| | Squalane | 0.6% w/v |
| | Nikkol DLP | 2.0 " |
| | Solulan 16 | 0.5 " |
| 35 | Crodafos N 3 N | 0.5 " |
| | Glycerin | 5 " |
| | Ethanol | 10 " |

Following substantially the same procedure as in the above Example 2, there is obtained
40 a transparent nourishing facial lotion.



or a salt thereof or a higher fatty alcohol-polyoxyethylene ether surface active agent of the general formula

EXAMPLE 4

| | | |
|----|---|----------|
| | Squalane | 3% w/v |
| | Crodafos N 3 N | 4 " |
| 45 | Magnesium salt of lauryl alcohol-ethylene oxide | |
| | sulfuric acid | 40 " |
| | (Texapon MG, Registered Trade Mark, of Henkel International G.M.B.H., Germany) | |
| 50 | Perfume | Optional |

55 The mixture of the squalane, the Crodafos and the Texapon is warmed to about 60°—70°C. and water (at about 60°—70°C.) is added thereto with stirring. After cooling, the perfume is added the mixture, and water is added to make up total 100% w/v. A transparent cleansing facial lotion is obtained.



wherein each of R and R' represents a saturated or unsaturated aliphatic hydrocarbon radical of 10 to 18 carbon atoms, n is an integer from 3 to 10, x is an integer from 1 to 3, and y is an integer from 8 to 40, and (c) a liquid diluent. 90

2. A composition according to Claim 1, wherein the surface-active agent is present in an amount from $\frac{1}{2}$ to 6 parts by weight per part by weight of the squalene compound. 95

3. A composition according to Claim 1 or 2, which contains 0.1 to 10% w/v of the squalene compound.

4. A composition according to any one of Claims 1 to 3, wherein the surface-active agent is a phosphoric acid ester type or higher fatty alcohol-polyoxyethylene glycol ester type surface-active agent specifically identified herein.

5. A composition according to Claim 1 substantially as hereinbefore described.

6. A composition according to Claim 1 substantially as described in any one of the

5 Examples.

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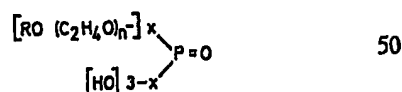
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We have now found that when a surface
35 active agent of the phosphoric acid ester type
or of the higher fatty alcohol-polyoxyethylene
ether type is added in small amount to a
transparent aqueous cosmetic solution, the
squalene compound can be solubilized easily
40 in said solution. The resulting transparent
solution can be added to any of those addi-
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losing its transparency.

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45 a flowable cosmetic composition which comprises (a) at least one of squalene, squalane

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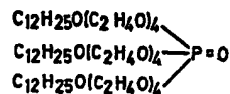
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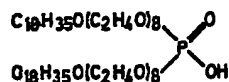
Pristane is aliphatic hydrocarbon of the empirical formula $C_{15}H_{32}$, which exists in the livers of fish, particularly shark, and has the same properties as those of squalane.

Typical surface active agents useful in this invention are illustrated below.

Phosphoric acid ester type 80

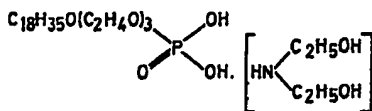


(Hostaphat KL 340, Registered Trade Mark, of Hoechst A.G., Germany)

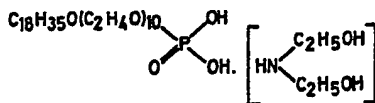


(Hostaphat KO 280),

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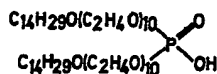


(Crodafos N3N, Registered Trade Mark, of Nippon Croda Co., Ltd., Japan)



(Crodafos N₁₀N)

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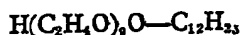


(Nikkol DLP 10, tradename of Nikko Chemicals Co., Ltd., Japan)

15 The salts of these phosphoric acid ester type surface active agents, for example, di-lower alkanolamine salts (e.g. diethanol amine salts) or alkali metal salts (e.g. sodium salts), also may be used.

Higher fatty alcohol-polyoxyethylene ether type

20



(Nikkol BL-9, from Nikko Chemicals Co., Ltd., Japan)



25 (Brij 96, Registered Trade Mark of Kao-Atlas Co. Ltd., Japan or Volpo 10, Registered Trade Mark, of Nippon Croda Co., Ltd., Japan)



(Brij 98, from Kao-Atlas Co., Ltd., Japan)

30



(Nikkol BL-15, from Nikko Chemicals Co., Ltd., Japan)



(Nikkol BL-25, tradename, of Nikko Chemicals Co., Ltd., Japan)

35

Mixture of higher fatty alcohol-polyoxyethylene glycol ethers

(Eumulgin M8, Registered Trade Mark of Henkel International G.M.B.H., Germany)

Polyoxyethylene lanoline alcohol ethers

40

(Solulan 16, tradename, of American Cholesterol Product Incorporation, U.S.A.)

The amount of the surface active agent to be used as a solubilizing agent for the squalene compound may vary depending on the type of said surface active agent but it usually is a small amount falling within the range of 1/2 to 6 parts per part by weight of the squalene compound. If the surface active agent is used in too large an excess, the resulting cosmetic will be a jelly, with poor fluidability, which has no commercial value. By the addition of said surface active agent, it is possible to obtain a transparent, liquid cosmetic containing 0.1—10% w/v of the squalene compound.

45

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It is very surprising that a transparent, flowable cosmetic having as high concentration of the squalene compound as about 10% w/v can be obtained using a small amount of the solubilizing agent. The resulting transparent, liquid cosmetic is a commercially valuable transparent cosmetic solution which is excellent in emulsifiability, penetration, hydrophilization, extendability, etc., whilst retaining the special effect of the squalene compound.

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The following examples illustrate the invention:

EXAMPLE 1

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| | |
|------------------|----------|
| Squalene | 1% w/v |
| Hostaphat KL 340 | 2 " |
| Glycerine | 5 " |
| Citric acid | 0.2 " |
| Sodium citrate | 0.2 " |
| Ethanol | 5 " |
| Perfume | Optional |

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The mixture of the squalene, the Hostaphat and perfume is warmed to about 70°—80°C. and a solution of the glycerine and the citric acid in water (at about 70°—80°C.) is gradually added thereto with stirring.

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To the resulting mixture is added the ethanol. Then, water is added in sufficient amount to make up total 100% w/v. A transparent nourishing facial lotion is obtained.

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EXAMPLE 2

| | | |
|----|------------------|-------------------------|
| | Squalene | 0.4% w/v |
| | Pristane | 0.2 " |
| | Crodafos N 10 N | 0.5 " |
| 5 | Volpo 10 | 1.0 " |
| | Solulan 16 | 0.5 " |
| | Allantoin | 0.05 " |
| | Propylene glycol | 5 " |
| | Methylparaben | 0.08 " |
| 10 | Propylparaben | 0.008 " |
| | Ethanol | 15 " |
| | Dyestuff | optional |
| | Lactic acid (5%) | optional to make pH 5.0 |

The mixture of the squalane, the pristane, the Crodafos and the Volpo is warmed to about 80°—90°C. To the warmed mixture is added about one-tenth volume of water (at about 80°—90°C.), based upon the total volume of the finished lotion, with stirring. After cooling, the resulting mixture is dissolved in the remaining portion of the water and to the solution is added a solution of the methylparaben and the propylparaben in the ethanol. Then, the allantoin, the propylene glycol and the Solulan are successively added to the mixture, which is then acidified to pH 5.0 by gradual addition of the lactic acid. Finally, water is added to make up total 100% w/v. A transparent nourishing facial lotion is obtained.

EXAMPLE 3

| | | |
|----|----------------|----------|
| | Squalane | 0.6% w/v |
| | Nikkol DLP | 2.0 " |
| | Solulan 16 | 0.5 " |
| 35 | Crodafos N 3 N | 0.5 " |
| | Glycerin | 5 " |
| | Ethanol | 10 " |

Following substantially the same procedure as in the above Example 2, there is obtained a transparent nourishing facial lotion.

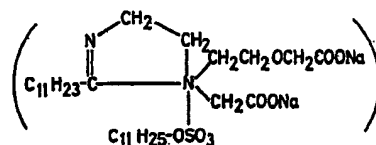
EXAMPLE 4

| | | |
|----|--|----------|
| | Squalane | 3% w/v |
| | Crodafos N 3 N | 4 " |
| 45 | Magnesium salt of lauryl alcohol-ethylene oxide sulfuric acid | 40 " |
| | (Texapon MG, Registered Trade Mark, of Henkel International G.M.B.H., Germany) | |
| 50 | Perfume | Optional |

The mixture of the squalane, the Crodafos and the Texapon is warmed to about 60°—70°C. and water (at about 60°—70°C.) is added thereto with stirring. After cooling, the perfume is added the mixture, and water is added to make up total 100% w/v. A transparent cleansing facial lotion is obtained.

EXAMPLE 5

| | | | |
|--|------------------------|--------|----|
| | Pristane | 3% w/v | 60 |
| | Eumulgin M8 | 4 " | |
| | Miranol 2 MCA modified | 30 " | |



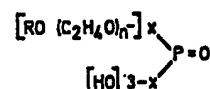
| | | | |
|--|-----------------|--------|----|
| | Hexylene glycol | 2% w/v | |
| | Amisol LDE | 1 " | 65 |

(Lauryl monoethanolamide, of Nikko Chemicals Co., Ltd., Japan)

The mixture of the pristane, the Eumulgin, the Mironal and the Amisol is warmed to about 60°—70°C. To the warmed mixture is added an aqueous solution of the hexylene glycol (at about 60°—70°C.) After cooling, water is added to make up total 100% w/v. A transparent shampoo is obtained.

WHAT WE CLAIM IS:—

1. A flowable cosmetic composition which comprises (a) at least one of squalane, squalene and pristane, (b) at least one phosphoric acid ester-type surface active agent of the general formula



or a salt thereof or a higher fatty alcohol-polyoxyethylene ether surface active agent of the general formula



wherein each of R and R' represents a saturated or unsaturated aliphatic hydrocarbon radical of 10 to 18 carbon atoms, n is an integer from 3 to 10, x is an integer from 1 to 3, and y is an integer from 8 to 40, and (c) a liquid diluent.

2. A composition according to Claim 1, wherein the surface-active agent is present in an amount from $\frac{1}{2}$ to 6 parts by weight per part by weight of the squalene compound.

3. A composition according to Claim 1 or 2, which contains 0.1 to 10% w/v of the squalene compound.

4. A composition according to any one of Claims 1 to 3, wherein the surface-active agent is a phosphoric acid ester type or higher fatty alcohol-polyoxyethylene glycol ester type surface-active agent specifically identified herein.

5. A composition according to Claim 1 substantially as hereinbefore described.

6. A composition according to Claim 1 substantially as described in any one of the

5 Examples.

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